SYNOPSIS

Nanoscience dominates almost all areas of science and technology in the 21^{st} century. Nanoparticles are of fundamental interest since they possess unique size dependent properties (optical, electrical, mechanical, chemical, magnetic etc.), which are quite different from the bulk and the atomic state. The research work presented in the thesis is on the preparation, characterization and studies on Ir, Os and graphene oxide-based systems. Interconnected Ir and Os nanochains are prepared under environmentally friendly conditions in aqueous media and subsequently used as substrates for surface enhanced Raman scaterring studies and also as electrocatalysts for oxygen reduction and formaldehyde oxidation. Ir and IrO_x nanostructures are prepared using borohydride at different temperatures. The nature of interaction of heme proteins with IrO_x is studied using spectroscopic techniques. Electrochemical studies on reduced graphene oxide include sensing of biomolecules with high sensitivity and oxygen reduction reaction (ORR) in aqueous alkaline medium. rGO is also used as support for anchoring Ir nanoparticles and the catalyst is used for the oxidation of benzyl amines to corresponding imines. The thesis is divided in to seven chapters and details are given below.

Chapter 1 gives an introduction about the synthetic strategies and properties of metal nanostructures. This is followed by literature survey on Ir, Os and graphene oxide-based systems relevant to the present study. Aim and scope of the present investigation is given at the end. Chapter 2 discusses the experimental procedures and characterization techniques used in the present study.

Chapter 3 involves the preparation, characterization and studies on interconnected Ir nanochains. Assemblies of small sized nanoparticles forming network-like structures have attracted enormous interest and different metal nanoassemblies have been reported using different procedures. Ir^{3+} reduction is kinetically not a very favourable process and hence there are not many attempts to synthesize Ir-based nanostructures. Assemblies of interconnected Ir nanoparticles have been synthesized in the present studies using borohydride as reducing agent and ascorbic acid as capping agent, at high temperatures. Polyfunctional capping molecules such as ascorbic acid and vitamin P play important role for the formation of network-like Ir nanostructures. Optical properties of the networks are probed using UV-Vis spectroscopy and evolution of coupled plasmon of Ir nanochains at 418 nm (figure 1) is observed. The nanochains are used as substrates for SERS studies while the catalytic activity is followed for the reduction of nitroaromatics. Electrocatalytic activity of Ir nanochains is exemplified using oxygen reduction and formaldehyde oxidation. Ir nanochains show better electrocatalytic activities than nanoparticles as shown in figure 2.

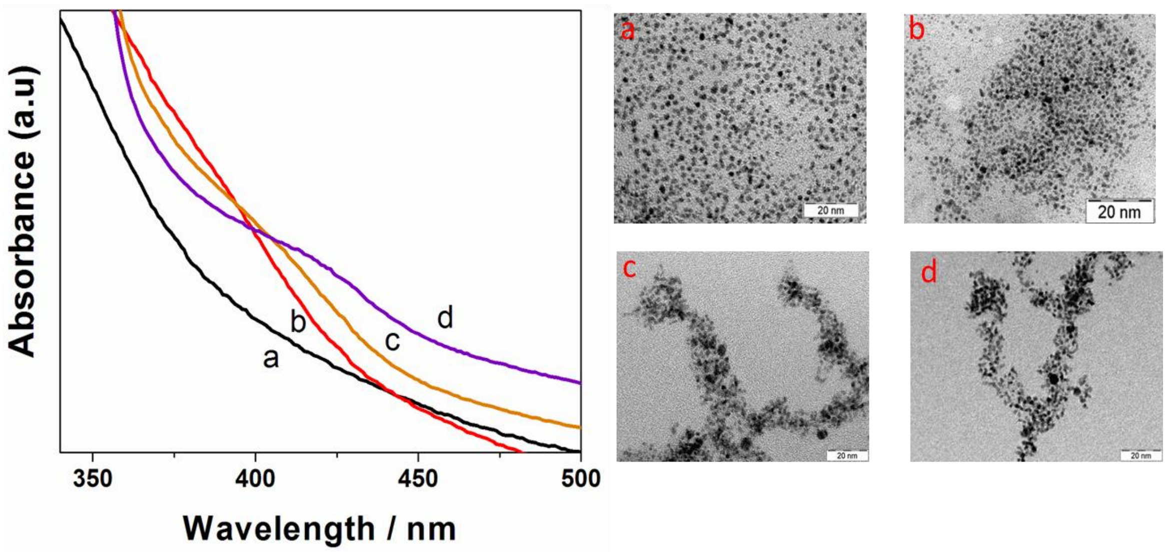

Figure 1. Time dependent UV-Vis absorption spectra of Ir nanoparticles recorded at various time intervals of (a) 5; (b) 15; (c) 30 and (d) 60 minutes of reduction of Ir^{3+} using borohydride and the corresponding TEM images.

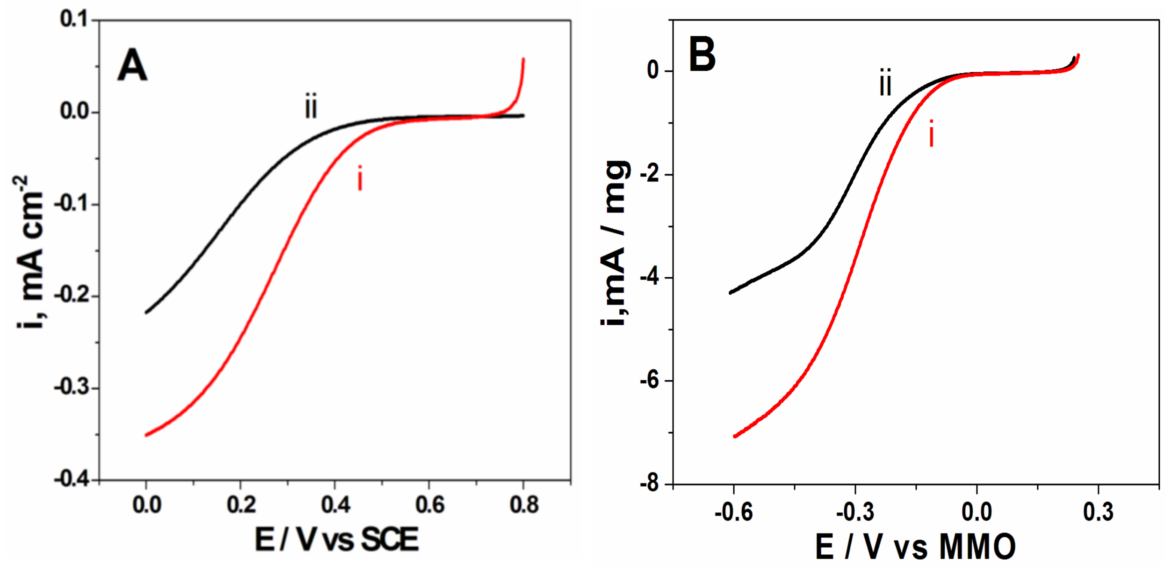

Figure 2. Polarization curves for oxygen reduction on (i) Ir nanochains and (ii) Ir nanoparticles in (A) 0.5 M H_2SO_4 and (B) 0.1 M KOH at a scan rate of 0.005 V/s. Rotation speed used is 1000 rpm.

Chapter 4 discusses the preparation of Ir and IrO_x using borohydride. The reaction temperature determines the product. Various physicochemical, microscopic and spectroscopic techniques have been used to understand the evolution of nanostructures. Borohydride reduces Ir^{3+} at high temperatures to form high surface area foams, while at 25°C, it results in an alkaline environment that helps in the hydrolysis of the Ir precursor to form IrO_x nanoparticles. Porous IrO_x is formed when Ir foams are annealed at high temperatures. Water oxidation has been demonstrated using IrO_x nanoparticles and foams. Biocompatibility of IrO_x is used to study the nature of interaction of heme proteins and the formation of bioconjugates using spectroscopic techniques. IrO_x forms bioconjugates with substantial changes observed in secondary and tertiary structures of proteins.

Chapter 5 explores the synthesis of interconnected ultrafine Os nanoclusters and the nanostructured materials are used as SERS substrates. Os nanochains are prepared under environmentally friendly conditions using polyfunctional molecules like ascorbic acid and vitamin P as both reducing agent and capping agent in aqueous media. Small sized (1-1.5 nm) Os nanoparticles spontaneously self-assemble to form clusters of few tens of nm that in turn self-organize to form branched nanochains of several microns in size. The as-formed nanochains show surface plasmon absorption in the visible region ~ 540 nm which make them active substrates for surface enhanced Raman scattering (SERS) studies. High SERS activity is observed for fluorescent analyte, rhodamine 6G and non-fluorescent analyte, mercaptopyridine, with different laser excitation sources. Efficient energy transfer from fluorescent R6G dye to Os nanochains is observed based on steady state and time resolved fluorescence measurements.

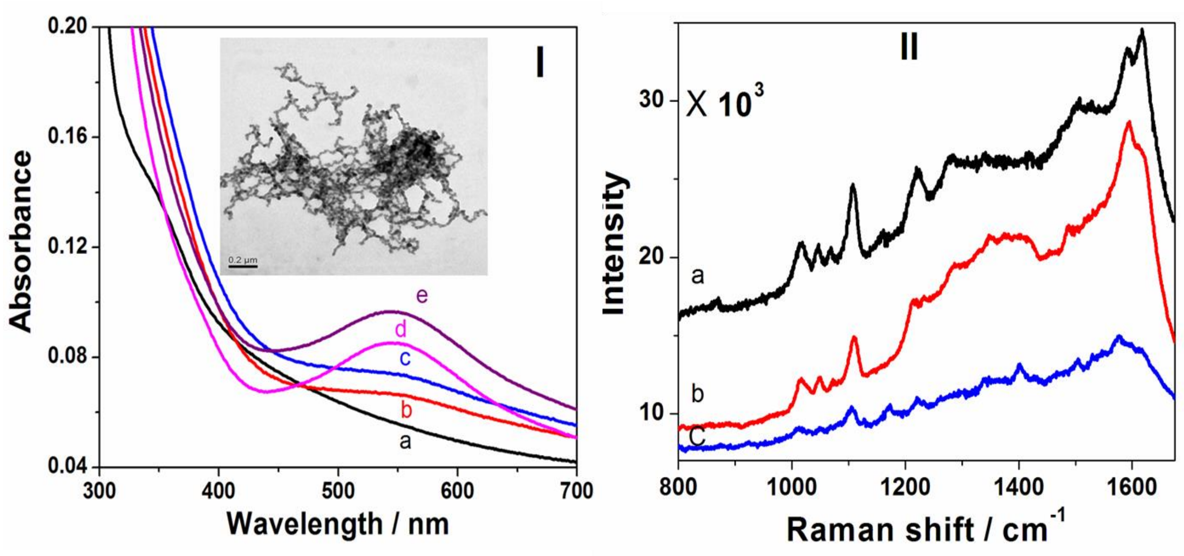

Figure 3. (I) Time dependent UV-Vis absorption spectra of Os nanochains recorded at different time intervals of (a) 5; (b) 7; (c) 15; (d) 30 and (e) 60 minutes. Inset shows the TEM images of Os nanochains after 60 minutes of reduction. (II) SERS spectra of 4-MPy adsorbed on Os nanochains from (a) 1 mM; (b) 10 µM and (c) 1 µM solutions using 514 nm laser excitation.

Chapter 6 discusses the studies based on reduced graphene oxide. Reduced graphene oxide (rGO) is explored as electrodes for simultaneous determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA) at low concentrations useful in medical diagnostics (figure 4A). It is also used as metal-free electrocatalyst for ORR (figure 4B). The use of rGO as a support for anchoring Ir nanoparticles is probed and subsequently the Ir/rGO is used as catalyst for direct aerobic oxidation of benzyl amine derivatives to corresponding imines.

Chapter 7 describes the summary of the work and scope for further studies.

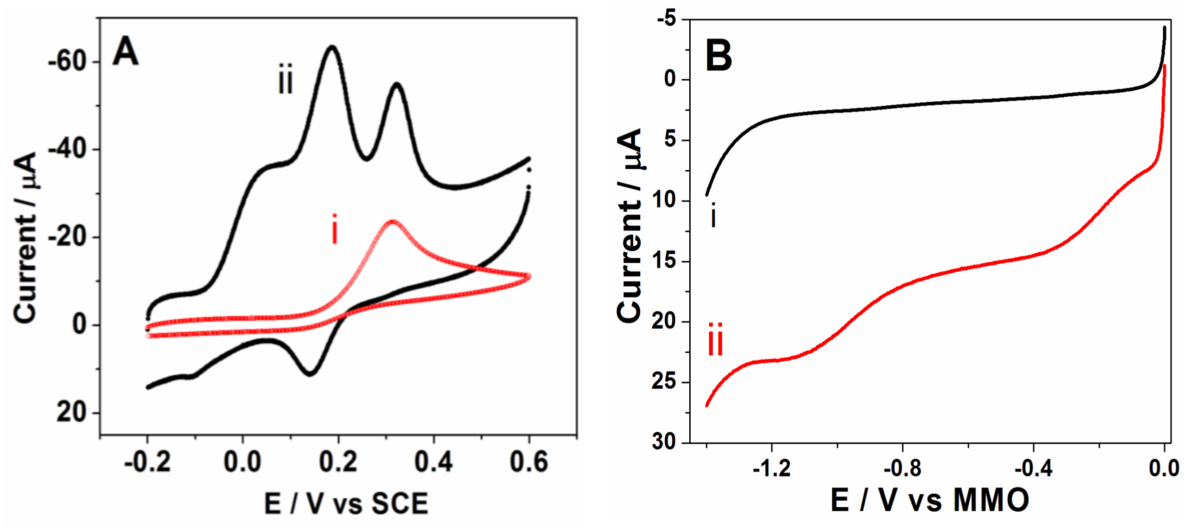

Figure 4. (A) Cyclic voltammograms of a mixture of 1 mM AA, 50 μM DA and 100 μM UA on (i) bare GCE and on (ii) rGO modified GCE in pH 7.2 solution. (B) Linear sweep voltammograms of rGO in (i) N_2 saturated (ii) O_2 saturated KOH (pH 14) at a scan rate of 0.005 V/s.

Appendix 1 discusses the preparation of different Ir nanostructures using simple galvanic displacement reaction on copper foil while appendix 2 describes the preparation of different sized Ir nanoparticles and their electrocatalytic activity towards oxygen reduction reaction.